Biological Water Gas Shift

DOE Hydrogen, Fuel Cell, and Infrastructure Technologies Program Review

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Process Overview

- In the Water-gas Shift (WGS) reaction, CO is oxidized to CO_2 while water is reduced to hydrogen:

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

- This process is used industrially to produce additional H_2 from synthesis gas streams using a 2-stage catalytic reactor (FeO/Cr at 450^{o}C, CuO/ZnO at 250^{o}C)
- Several strains of photosynthetic bacteria, isolated from the natural environment by NREL researchers, are able to perform the WGS reaction at ambient temperatures
- This may be an attractive alternative to conventional processes
  - Heat Integration Issues
  - Biological vs. Chemical Catalyst
  - Overall System Costs

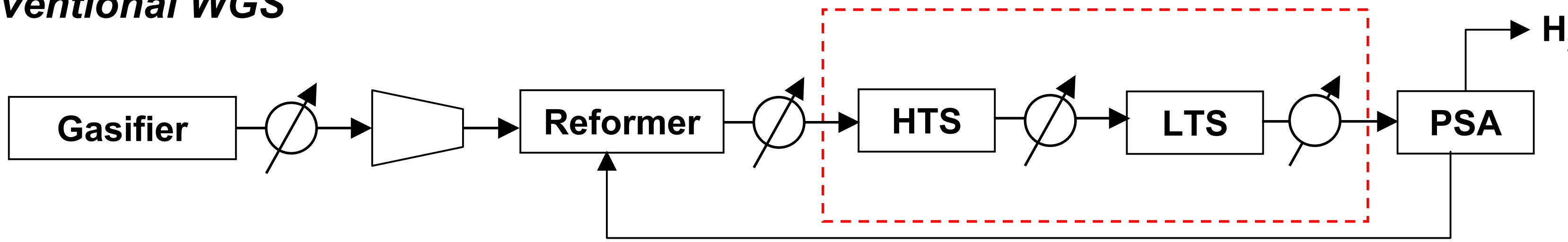
Relevance/Objective

Objective: to Improve Biological Water-Gas Shift (WGS) for Producing Biomass-Derived H_2.

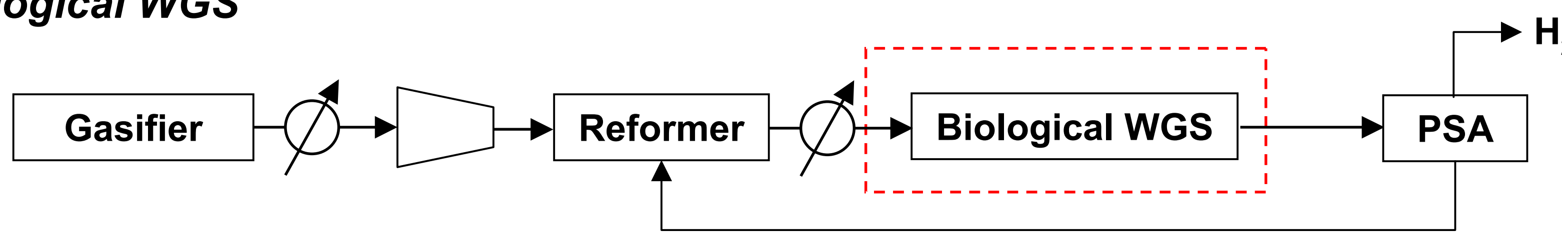
- Barrier H – Cost of Biomass-derived H_2
- Task 4 –Alternatives and Improvements to Conventional WGS
- Two Milestones
  - Verify operation of 100psi WGS Bioreactor (go/no go)
  - Demonstrate 100-L WGS Bioreactor

WGS Flow Chart - Conventional & Biological

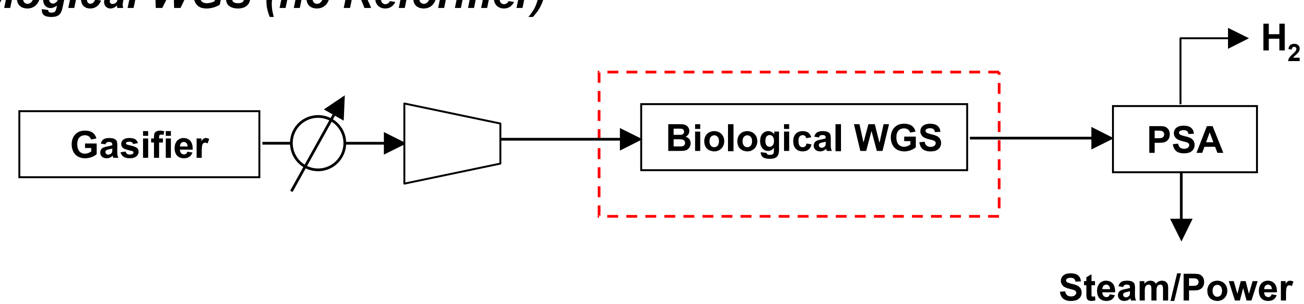
Conventional WGS



Biological WGS



Biological WGS (no Reformer)



Technical Approach

Key Challenges

- Physiology and Molecular Biology:
  - Increase specific water-gas shift rate
  - Eliminate induction period for water-gas shift
- Integrated Engineering and Operation:
  - Increase reactor productivity
  - Operate reactors at elevated pressures

Our Approach to Overcome these Challenges

- Understanding Leads to Solutions
- Physiology and Molecular Biology:
  - Understand the microbe's genetic system for genetic engineering
- Integrated Engineering and Operation:
  - Understand high-pressure bioreactor dynamics

Project Timeline - Biology

Project Steps	FY99	FY00	FY01	FY02	FY03
Improved CO shift rate by more than **5** fold by improving CO mass transfer					
Demonstrated O_2 tolerance of the hydrogenase; half-life of **21 hours** in full air					
H_2 was produced from **water** in a linked cyanobacterial-hydrogenase hybrid system					
Isolated mutants and cloned **2** water-gas shift genes					
Cloned **8** genes in the water-gas shift – manipulate genes to improve H_2 production					

Accomplishment 1:
Cloned 9 Genes in Water-gas Shift Reaction

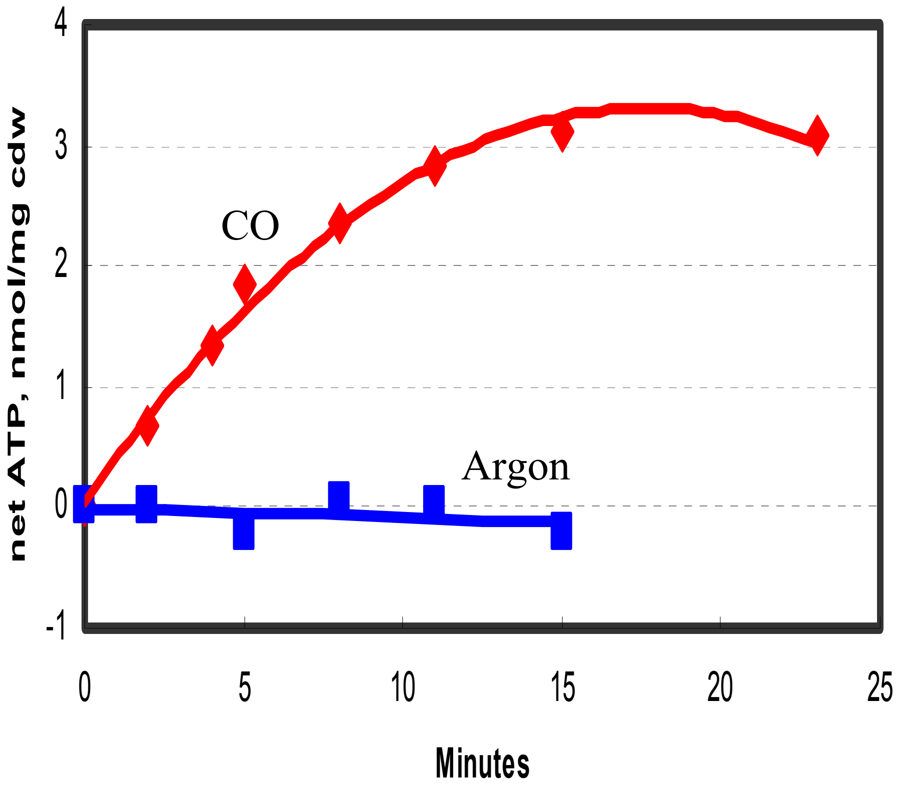
$$CO + H_2O \xrightarrow{\textit{coo}\ \text{F, S, C}} CO_2 + 2e^{-1} + 2\,H^+$$

$$2\,H^+ + 2e^{-1} \xrightarrow{\textit{coo}\ \text{M, K, L,X, U, H}} H_2$$

- 9 water-gas shift genes are completely sequenced
- WGS-genes complementation was successful, which could lead to over-expression of WGS activity
- With sequences known, these genes can be manipulated to improve H_2 production

➢ Meeting FY03 milestone of understanding genetic system of CO shift to allow for manipulations to increase H_2 production

Accomplishment 2:
Water-gas Shift Yields Energy in Darkness



- CO supports both cell growth and ATP synthesis, in darkness
- ATP can be used to regenerate more water-gas shift catalysts in darkness
- Dark bioreactor simplifies reactor design, operation, and reduces cost

Addressing Review Panel's comments that shift reaction can support cell growth yielding energy in darkness leading to sustained H_2 production

Project Timeline - Engineering

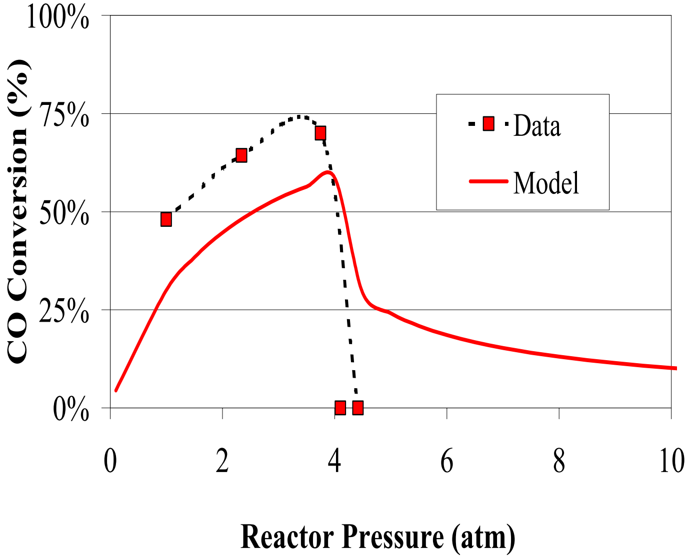
Project Steps	FY99	FY00	FY01	FY02	FY03
Test new biological WGS reactor designs					
Evaluate improved reactor internals					
Condition biomass-derived syngas; Demonstrate bioreactor operation at 5-L scale					
Operate bioreactor at P=10 atm; Measure shift kinetics of *Rx. gelatinosus*					
Determine Cause of Elevated Pressure Inhibition of WGS Reaction					

- This project has a go/no go decision in FY06 to verify 100 psi operating pressure water-gas shift bioreactor at 95% CO conversion efficiency

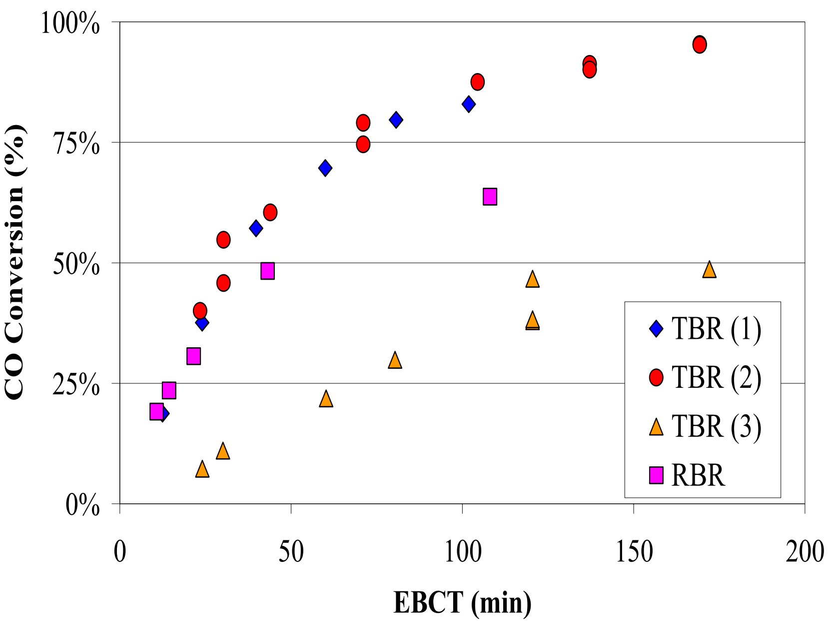
Accomplishment 3:
Elevated Pressure Bioreactor Operation

- Trickle Bed Reactor (TBR) provided good gas-liquid mass transfer, but was difficult to control and analyze
- Developed a novel Recirculating Bubble-Column Reactor (RBR) which provides good gas-liquid mass transfer, and is easier to control and analyze

RBR Design Provides Stable Operation at Elevated Pressure

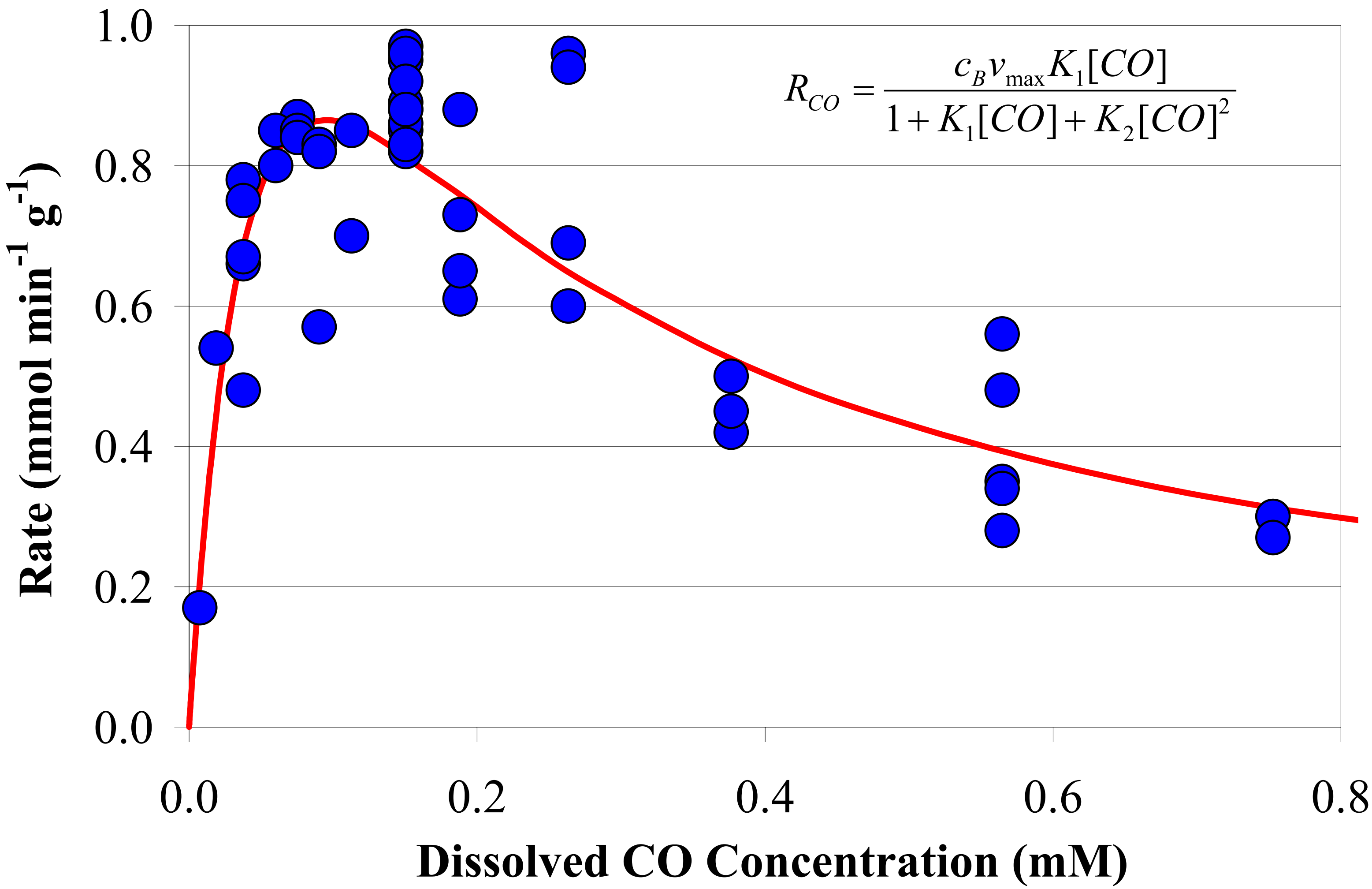


- *Laboratory facilities can accommodate five parallel 1-L bioreactors at pressures up to 20 atm with automated GC analysis of inlet & outlet streams*



Accomplishment 4:

Intrinsic Bacterial Kinetics of *Rx. gelatinosus* CBS show Inhibition at Elevated [CO]



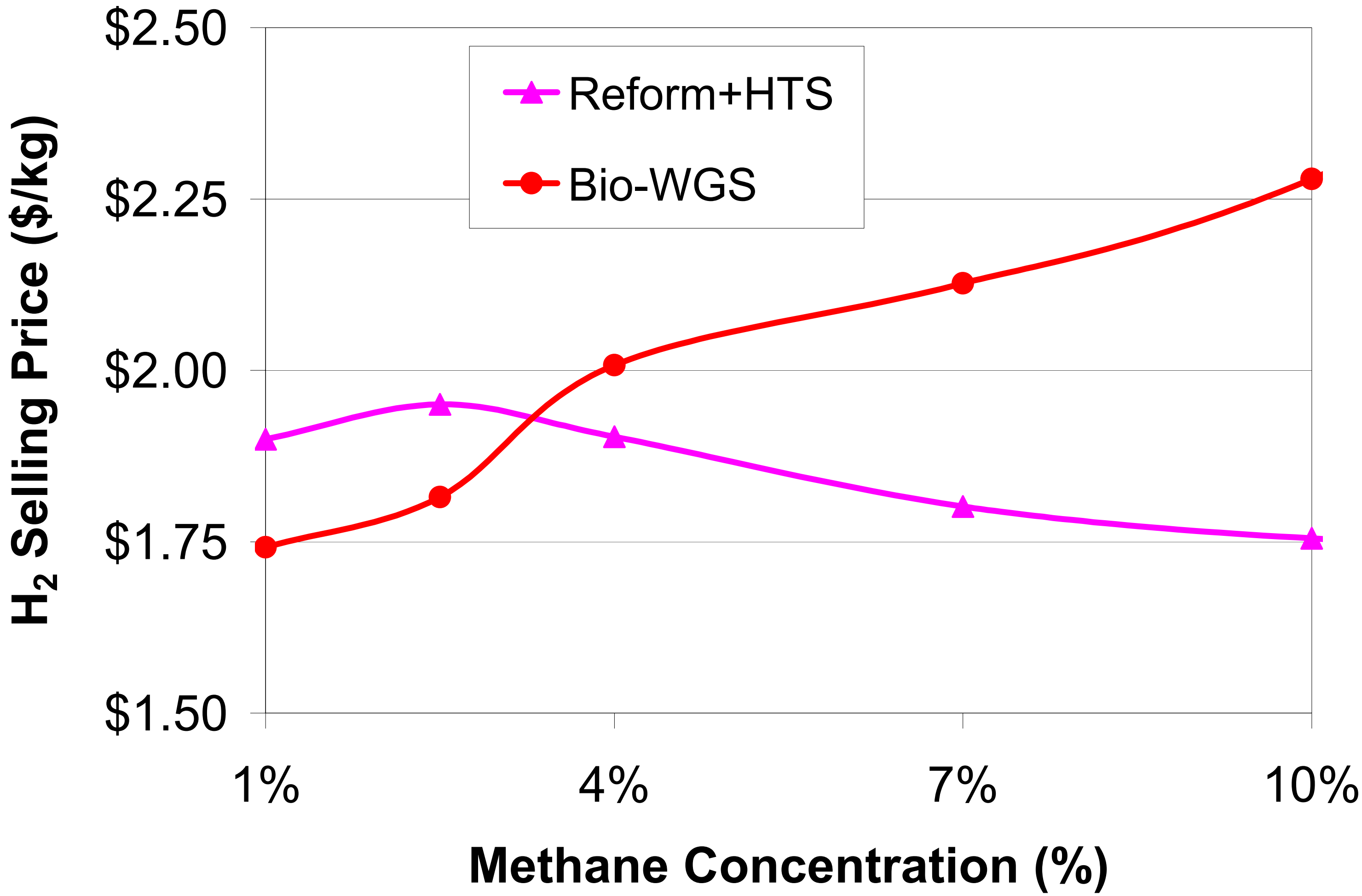
Collaborations/Industry Interactions

- Collaborations
  - Washington State University
    - Fundamental studies on the energetics of the water-gas shift pathway
  - University of Victoria (Canada)
    - Proteomics-based investigations of the water-gas shift pathway
- Industry Interactions via Work for Others
  - Oil Refinery Service Co.
    - Convert CO in refinery gas to additional hydrogen via biological water-gas shift

Publications

- Maness and Weaver. 2002. “Hydrogen production from a carbon-monoxide oxidation pathway in *Rubrivivax gelatinosus*.” *International J. Hydrogen Energy*. 27: 1407-1411.
- Merida, Maness, Brown, and Levin. “Enhanced hydrogen production from indirectly heated biomass, and removal of carbon gas emission using a novel biological gas reformer. Manuscript. Accepted for publication in *International J. Hydrogen Energy*.
- Watt, Huang, Smolinski, Maness and Wolfrum. “The water-gas shift pathway in *Rubrivivax gelatinosus*.” Manuscript in preparation.
- Wolfrum, Watt, Amos “Bioreactor Design Studies at Elevated Pressures”, Manuscript in Preparation.
- Abstracts submitted for presentation at “12th Western Photosynthesis Conference” and “25th Symposium on Biotechnologies for Fuels and Chemicals.”

Comparison of Conventional vs. Biological Water-Gas Shift; Reforming Controls Choice



Results of Techno-Economic Analysis

- The biological water-gas shift reaction (like other biological processes) is slower than the corresponding catalytic process
- The biological reactor will inevitably be larger than the corresponding chemical reactor
- Overall cost savings result from balance-of-plant considerations
- For the biological WGS process, savings result from avoiding steam reformer & associated equipment

Plans and Future Milestones - Biology

- The hydrogenase enzyme system from *Rubrivivax gelatinosus* is unique in its high rate of hydrogen evolution and its tolerance to oxygen, <u>unlike any other hydrogenases reported in literature</u>
- Continued molecular biological study of this organism could lead to other applications:
  - genetic transfer of the hydrogenase into a cyanobacterium (blue-green alga) to produce hydrogen from **water**
  - a two-stage "fermentation/photofermentation" process to convert biomass to hydrogen via fermentation and the low-value waste organic acids from which are converted into additional hydrogen in a second-stage photofermentation reaction
  - high-value co-product generation during hydrogen production
- *Milestone: increasing WGS activity two-fold through genetic engineering*

Plans and Future Milestones - Engineering

- Elevated-pressure bioreactor operation with gaseous substrates is a unique research area
- Continued research in this area could lead to process improvements and other applications:
  - niche applications for low-HC syngas streams
  - elevated pressure reactor stability issues
  - coproduct production (e.g., SCP, PHA)
  - reactor engineering for two-stage "fermentation/photofermentation" process
- *Milestone: long-term operation of laboratory-scale elevated pressure bioreactors (>4 months)*

Reviewers' Comments - Biology

- *Try to understand water-gas shift metabolic pathway and probe the genes*
  - 9 genes have been sequenced, which will be used to construct a water-gas shift metabolic pathway and to conduct genetic engineering to increase hydrogen production (accomplishment 1)
- *Demonstrate growth and energy generation in darkness*
  - We confirmed that CO supports both cell growth and ATP synthesis in darkness, both of which could sustain hydrogen production (accomplishment 2)
  - More robust dark bioreactor would lower cost of hydrogen
- *Determine lower limit to which water-gas shift can be driven by the biological system even though commercial operation may not work near this limit*
  - water-gas shift rates were determined in various CO concentrations. Results indicated that at 3.6% gaseous CO (26 μM dissolved), water-gas shift rate is 50% maximum (accomplishment 4)

Reviewers' Comments - Engineering

- *Is pH causing inhibition at elevated pressures?*
  - No; experiments with buffer disprove this; likely substrate or product inhibition
- *What will the reactor(s) look like? Low-cost reactors inconsistent with elevated pressure operation*
  - Biological reactors will be larger than corresponding high-temperature catalytic reactors; Cost savings may result from less-expensive materials, but balance-of-plant costs will likely control economics